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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

**PUBLICATIONS/PATENTS/PRESENTATIONS
HONORS/STUDENTS
REPORT**

for

Grant N00014-91-J-1447

R&T Code 4134044

**OMVPE Growth of InAsSbBi and Related Alloys Using New
Organometallic Group V Sources**

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and Electrical Engineering
University of Utah
Salt Lake City, Utah 84112**

1 June 1992

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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 4134044

Contract/Grant Number: N00014-91-J-1447

Principal Investigator: G.B. Stringfellow

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Summary of Activities During the Last 12 Months.

- a. Number of papers submitted, unpublished: 9.
- b. Number of papers in refereed journals: 7.
- d. Number of papers published in books: 1.
- h. Number of Invited presentations at professional meetings: 7.
- i. Number of presentations at professional meetings: 4.
- j. Honors/Awards/Prizes: 11.
- k. Number of students supported: 3.
(no minority or female students, 2 Asian graduate students)
- l. Other Funding: -- G.B. Stringfellow

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AGENCY	TITLE	DATES	ANNUAL \$	P.I. Man Months/Yr.
G.B. Stringfellow				
D.O.E.	Theoretical and Experimental Study of Solid Phase Miscibility Gaps in III/V Quaternary Alloys	4/1/92- 3/31/93	\$84,841	2.0
AFOSR	Use of D ₂ to Elucidate OMVPE Growth Mechanisms	10/1/91- 9/30/92	\$40,000	0.67
ARO	New Sources for Chemical Beam Epitaxy (Note: The lead P.I. on this project is Prof. L. Sadwick, Department of Electrical Engineering. My role in the project is relatively minor.)	6/1/91- 5/30/92	\$88,223	0.67
R.M. Cohen				
N.S.F.	Study of Diffusion Mechansims in GaAs	10/91- 9/92	\$95,000	1.0

Part I (Supported Exclusively by ONR Unless Indicated).

a. Papers Submitted to Refereed Journals (not yet published)

Novel Precursors for Organometallic Vapor Phase Epitaxy (Invited Paper, ICCG-10), G.B. Stringfellow, J. Crystal Growth (to be published) (ONR, AFOSR, ARO).

Tertiarybutyldimethylantimony for InSb Growth, C.H. Chen, K.T. Huang, D.L. Drobeck, and G.B. Stringfellow, J. Crystal Growth (submitted for publication).

Tertiarybutyldimethylantimony: A New Antimony Source for Low Temperature OMVPE Growth of InSb, C.H. Chen, K.T. Huang, and G.B. Stringfellow, Appl. Phys. Lett. (accepted).

Triisopropylindium, a New Precursor for OMVPE, C.H. Chen, C.T. Chiu, and G.B. Stringfellow, J. Crystal Growth, (submitted). (ONR, ARO).

Triisopropylindium: Decomposition Study and Use for Low Temperature Growth of InAs, C.H. Chen and G.B. Stringfellow, J. Crystal Growth, (submitted). (ARO, ONR).

Decomposition Studies of TBDMSb, D.S. Cao, C.H. Chen, C.W. Hill, S.H. Li, G.B. Stringfellow, D.C. Gordon, D.W. Brown, and B.A. Vaartstra, J. Electron. Mater. (accepted). (ONR, AFOSR).

Decomposition Studies of Triisopropylantimony and Triallylantimony, S.H. Li, C.A. Larsen, G.B. Stringfellow, and R.W. Gedridge, J. Electron. Mater. (accepted). (AFOSR, ONR).

b. Papers Published in Refereed Journals

Fundamental Aspects of Vapor Growth and Epitaxy, G.B. Stringfellow, J. Crystal Growth 115, 1 (1992). (DOE, ONR, AFOSR).

Ultra-Low Temperature OMVPE of InAs and InAsBi, K.Y. Ma, Z.M. Fang, R.M. Cohen, and G.B. Stringfellow, J. Electron. Mater. 21, 143 (1992).

Effect of Growth Temperature on Photoluminescence of InAs Grown by OMVPE, Z.M. Fang, K.Y. Ma, R.M. Cohen, and G.B. Stringfellow, Appl. Phys. Lett. 59, 1446 (1991).

Investigation of Organometallic Vapor Phase Epitaxy of InAs and InAsBi at Temperatures as Low as 275°C, K.Y. Ma, Z.M. Fang, R.M. Cohen, and G.B. Stringfellow, J. Appl. Phys. 70, 3940 (1991).

OMVPE Growth of AlGaSb and AlGaAsSb, D.S. Cao, Z.M. Fang, and G.B. Stringfellow, J. Crystal Growth 113, 441 (1991). (AFOSR, ONR).

Triisopropylantimony for OMVPE of GaSb and InSb, C.H. Chen, Z.M. Fang, and G.B. Stringfellow, Appl. Phys. Lett. 58, 2532 (1991).

The Use of Triisopropylantimony for the Growth of InSb and GaSb, C.H. Chen, Z.M. Fang, and G.B. Stringfellow, J. Appl. Phys. 69, 7605 (1991)

d. Papers Submitted or Published in Books

New Sources for OMVPE, Record of Alloy Semiconductor Physics and Electronics Symposium, G.B. Stringfellow, Nagoya, Japan, (1991) pp.3-14. (ONR, AFOSR).

Comparison of Epitaxial Growth Techniques for III/V Layer Structures, Proceedings of Croissance de cristaux et de couches epitaxiales a applications electroniques et optiques, G.B. Stringfellow, Invited Paper (accepted for publication). (DOE, ONR, AFOSR)

Thermodynamic and Kinetic Aspects of III/V Epitaxy, Proceedings of Croissance de cristaux et de couches epitaxiales a applications electroniques et optiques, G.B. Stringfellow, Invited Paper (accepted for publication). (DOE, ONR, AFOSR).

Basic Principles of OMVPE, Proceedings of 8th International School on Crystal Growth (submitted). (DOE, ONR, AFOSR).

**h. Invited Presentations at Topical or Scientific/Technical Society Conferences
(all Delivered by G.B. Stringfellow).**

New Sources for OMVPE, 10th Symposium on Alloy Semiconductor Physics and Electronics, July 18-19, 1991, Nagoya, Japan (Plenary Talk).

Fundamental Aspects of Vapor Growth and Epitaxy, 7th International Conference on Vapor Growth and Epitaxy, July 15-17, 1991, Nagoya, Japan (Lead-Off Plenary Talk).

Thermodynamic & Kinetic Aspects of III-V Epitaxy, Croissance de cristaux et de couches epitaxiales a applications electroniques et optiques, Valais, Switzerland, March 15-21, 1992.

Comparison of Epitaxial Techniques for III-V Layer Structures, Croissance de cristaux et de couches epitaxiales a applications electroniques et optiques, Valais, Switzerland, March 15-21, 1992.

CVD Growth With Novel Precursors, 1992 Gordon Research Conference, The Chemistry of Electronic Materials, Ventura, CA, 2-6 March 1992.

Novel Precursors for Organometallic Vapor Phase Epitaxy, 10th International Conference on Crystal Growth, San Diego, CA, August 16-22, 1992.

Organometallic Vapor Phase Epitaxy, International Crystal Growth Summer School, Palm Springs, CA, August 9-14, 1992.

i. Contributed Papers

Use of the Newly-Developed Triisopropylindium for OMVPE Growth of InAs, (C.H. Chen, C.T. Chiu, and G.B. Stringfellow) 6th International Conference on MOVPE, Boston, June 1992.

Low-Temperature InSb Growth Using a New Sb Source: Tertiarybutyldimethylantimony, C.H. Chen, K.T. Kuang, D. Drobeck, G.B. Stringfellow, D.C. Gordon, D.W. Brown, and B.A. Vaartstra, 6th International Conference on MOVPE, Boston, June 1992.

Organometallic Vapor-Phase Epitaxial Growth of AlGaSb and AlGaAsSb, D.S. Cao, Z.M. Fang, and G.B. Stringfellow, 1991 Electronic Materials Conference, Boulder, CO, June 19-21, 1991.

Ultra-Low Temperature Organometallic Vapor-Phase Epitaxial Growth of InAs and InAsBi, K.Y. Ma, Z.M. Fang, R.M. Cohen, and G.B. Stringfellow, 1991 Electronic Materials Conference, Boulder, CO, June 19-21, 1991.

j. Honors

G.B. Stringfellow, Editorial Board, Materials Letters, 1989-present

G.B. Stringfellow, Associate Editor, Journal of Crystal Growth, 1979-present.

G.B. Stringfellow, Editorial Board, Journal of Electronic Materials, 1979-present.

G.B. Stringfellow, Treasurer: American Committee Organizing Committee for the International Symposium on GaAs and Related Compounds.

G.B. Stringfellow, Organizing Committee, Sixth U.S. OMVPE Workshop, April, 1993.

G.B. Stringfellow, Program Committee, 19th International Symposium on GaAs and Related Compounds, Karuizawa, Japan, September 28, 1992.

G.B. Stringfellow, Program and Publication Chairman, 18th International Symposium on GaAs and Related Compounds, Seattle, September, 1991.

- G.B. Stringfellow, Organizing Committee and Proceedings
Chairman, 6th International Conference on MOVPE,
Boston, June 1992.**
- G.B. Stringfellow, International Advisory Committee, First
International Symposium on Atomically Controlled Surfaces
and Interfaces, Tokyo, Japan, November, 1991.**
- G.B. Stringfellow, Program Committee, 10th International
Conference on Crystal Growth, San Diego, CA, August 16-22,
1992.**
- G.B. Stringfellow, International Advisory Board, International
Conference on Vapor Growth and Epitaxy, Nagoya, Japan,
July, 1991.**
- G.B. Stringfellow, International Advisory Committee, 3rd
International Conference on Chemical Beam Epitaxy,
University of Oxford, 1-5 September, 1991.**

k. Number of Graduate Students Receiving Support on ONR Grant

4 PhD students supported more than 25%.

Part II

Principal Investigator: G.B. Stringfellow

Cognizant ONR Scientific Officer: Dr. John C. Pazik

Telephone Number: (801)581-8387

Description of Project:

The major goal of the project is the organometallic vapor phase epitaxial (OMVPE) growth of a new III/V alloy, InAsSbBi, with a band gap of <0.1 eV at 77°K. This material is expected to be useful for infrared detectors with response in the wavelength range from 8 to 12 microns. The alloy is metastable, but for certain growth conditions it can be produced by OMVPE. This requires very low growth temperatures of 250-350°C. This, in turn, requires that new organometallic In and Sb precursors be developed which pyrolyze at lower temperatures than the conventional sources trimethylindium (TMIn) and trimethylantimony (TMSb).

A related goal is to produce materials suitable for device fabrication. The major problem with low temperature growth using the current precursors is the high levels of carbon contamination. Since carbon is a donor in these materials, this gives rise to high free electron concentrations. The use of novel precursors, not containing methyl radicals, is expected to solve this problem. Trimethylbismuth (TMBi) has been synthesized and used as the Bi precursor to date. In the future, other Bi precursors not containing methyl radicals may have to be used to produce material with acceptable carbon contamination levels.

Significant Results:

During the last year, the project has concentrated on the testing of new In and Sb precursors for the low temperature growth of InAs, GaSb, and InSb. A major effort has been made to produce high quality materials. This includes measuring the photoluminescence, electrical transport properties, and, in particular, the carbon doping levels using Hall effect and SIMS analysis.

Two new Sb precursors are particularly promising based on the initial studies. Both triisopropylantimony (TIPSb) and tertiarybutyldimethylantimony (TBDMSb) have been successfully used for the low temperature growth of InSb. Both precursors pyrolyze at approximately the same temperatures in an ersatz reactor. The value of T_{50} is approximately 300 C for both, 200 C lower than the value of 500 C measured in the same apparatus for TMSb. Thus, both are suitable for low temperature growth. The vapor pressure for TBDMSb is much higher than for TIPSb, which makes it more promising.

The OMVPE growth results indicate that TBDMSb allows the growth of InSb at temperatures as low as 350 C using low V/III ratios, about 50 C lower than for TIPSb. In addition, the range of V/III ratio over which acceptable morphologies are obtained is larger using TBDMSb. Since the TBDMSb contains two methyl radicals, we were concerned that unacceptable carbon doping levels might result. However, the studies of the pyrolysis mechanism, using the ersatz reactor, indicate that methyl radicals are not produced. The dimethylantimony intermediate pyrolyzes via a disproportionation reaction resulting in TMSb and Sb metal. At low temperatures the TMSb will not pyrolyze, so low carbon doping levels may be possible. The epitaxial layers of InSb produced using both precursors are n-type with free electron concentrations in the mid- 10^{16} cm⁻³ range for growth at 400°C. This indicates that C doping is not a major problem with either precursor.

Both ethyldimethylindium (EDMIn) and triisopropylindium (TIPIIn) have been used, with arsine, for the growth of InAs layers. Both allow growth at low temperatures than for TMIn. In addition, both allow the growth of high PL intensity InAs at lower (by 50°C) temperatures than for TMIn. Replacing TMIn with EDMIn has virtually no effect on carbon contamination. However, significantly, TIPIIn allows the low temperature growth of InAs layers with approximately 100 times lower carbon concentrations, as measured by both Hall effect and SIMS techniques. The use of either EDMIn or TIPIIn also leads to higher InAs growth efficiencies at low growth temperatures. However, parasitic reactions reduce the growth efficiency at higher growth temperatures for TIPIIn, making this precursor more promising for low pressure OMVPE and chemical beam epitaxy (CBE) applications.

It should be mentioned that R. Gedridge has synthesized the TIPSb and TIPIIn, under a separate ONR contract. The TBDMSb was synthesized by Advanced Technology Materials (ATM). Both the TIPSb and TBDMSb are now commercially available from ATM. The EDMIn comes from CVD.

In parallel with this effort, we have been working to increase the growth temperature at which we can obtain InAs_{0.94}Bi_{0.06} alloys. We have succeeded in increasing the temperature to approximately 350°C. This yields InAs with considerably better photoluminescence intensities and InAsBi with narrower x-ray diffraction peaks, indicative of improved crystalline perfection. We have also been constructing a new OMVPE apparatus specifically for the purpose of growing InAs/InSb monolayer superlattices, which offer promise for long wavelength detectors without the addition of Bi to the system.

Plans for Next Year:

Several sub-projects will proceed in parallel, all directed to the low temperature growth of InAsSbBi with a band gap of 0.1 eV, or less, and with carbon doping levels of $\leq 10^{17}$ cm⁻³, the lowest level that appears reasonable given the non-electronic grade of both precursors.

- i) Carbon doping in InSb is much less of a problem than for InAs, presumably due to the lower C-Sb bond strength as compared with that for C-As. Even using TMIn and TMSb, free electron concentrations of $\leq 10^{17} \text{ cm}^{-3}$ have been obtained in this work. Thus, the simplest approach will be the use of EDMIn or TMIn and TBDMSb for the growth of InSb containing Bi. Only about 2% Bi is required to reduce the band gap to the desired value of 0.1 eV. In the past, this approach has faltered because of the high temperatures required for TMSb pyrolysis. Lowering the temperature by 100°C, allowed by the use of TBDMSb and EDMIn, may allow us to reach the required Bi concentrations. Ultimately, we will add a small amount of TBAs, to obtain As concentrations (6%) necessary for lattice matching to the InSb substrate to be obtained.
- ii) The use of TIPIIn and TBAs for the low temperature growth of InAs, with the objective of obtaining the required low carbon doping levels. Subsequently, TMBi will be added, to produce $\text{InAs}_{0.94}\text{Bi}_{0.06}$. TIPBi may ultimately be required to give low carbon contamination levels.
- iii) Simultaneously, we are completing the construction of a new reactor suitable for the growth of (111) InAs/InSb monolayer superlattice structures. These are predicted theoretically to have band gaps of <0.1 eV.

Personnel:

3 graduate students will be supported by the ONR contract during the next year: Kuo-Tai Huang, Johngeon Shin, and Kenny Chiu. Three students supported 25% or more by the contract during the last year received their degrees during the last year, Kevin Ma and Zhong-Ming Fang received PhD degrees in Materials Science and Engineering, and Duenhua Jaw received his PhD degree in Electrical Engineering.

Part III.

Parts a-c (attached)

d. Description

InAsSbBi alloys with 6.1% Bi have been produced by OMVPE. These materials should be useful for infrared detectors with wavelength response extending to 12 μm . However, these high Bi concentrations can only be grown at low temperatures, 275-350°C. OMVPE growth is difficult using the conventional precursors trimethylindium (TMIn), arsine, and trimethylantimony (TMSb). In addition, the carbon contamination levels for these low-temperature InAsBi layers are unacceptably high. A promising approach to the solution of both problems is the development of new precursor molecules to replace TMIn and TMSb. This slide shows the optimum values of the ratio of input molar flow rates of the Sb precursors and TMIn (the V/III ratio) versus substrate temperature. Data are shown for two promising Sb precursors, triisopropylantimony (TIPSb) and tertiarybutyldimethylantimony (TBDMSb). Both precursors pyrolyze rapidly even at low temperatures, so are much superior to TMSb, with TBDMSb being somewhat better. In addition, the TBDMSb vapor pressure is more favorable. The resulting InSb layers have carbon contamination levels of less than 10^{17} cm^{-3} .

InAsSbBi for Infrared Detectors
G.B. Stringfellow/University of Utah

OBJECTIVE:

Grow New Material -- InAsSbBi
12 μm band gap at 77°K -- For infrared detectors

PROBLEMS:

Maximum Wavelength for InAsSb - 8 μm
Bi Has Very Low Solubility in InAs and InSb
Solubility Increases at Temperatures Much Less
Than Normal OMVPE Growth Temperatures

APPROACH:

Organometallic Vapor Phase Epitaxy (OMVPE)
Proven for metastable alloys at low temperatures
Sources - TMI_n, EDM_n, or TIP_n*
TMS_b, TIPS_b* or TBDMS_b*
TMB_i or TIP_{Bi}*
AsH₃ or tertiarybutylarsine (TBAs)
Note: * Denotes new precursor molecule
Temperatures -- 275-400C

RESULTS:

Demonstrated Bi concentrations of 6.1% in InAs,
Lattice constant expands with Bi addition
Therefore, it must be a solid solution
Requires very low growth temperatures
This gives carbon doping of 10^{19} cm^{-3}
Thus, require new In and Sb sources
Triisopropylantimony (TIPS_b), tertiary-
butyldimethylantimony (TBDMS_b), and
triisopropylindium (TIP_{In}) are promising.

InAsSbBi for Infrared Detectors
G.B. Stringfellow/University of Utah

CURRENT STATUS:

Have Produced InAsBi with 6.1% Bi
Using trimethyl-In and ethyldimethyl-In
Predicted Band Gap of 0.1 eV (12 μm) at 77°K
Growth Temperature 275-350°C
Heavily Carbon Contaminated (10^{19} cm^{-3})
Due to 3 Methyl Radicals on In Precursor
Prevents Demonstration of 0.1 eV Bandgap

1 YEAR PLAN:

Grow InSb $_{1-x}$ Bi $_x$ with $x=0.02$ and Low Carbon
Tertiarybutyldimethylantimony
+ ethyldimethylindium
Add 6% As, to Lattice Match InSb Substrates
Use New In and Sb Precursors for Growth of
InAs $_{1-x}$ Bi $_x$ with $x \geq 0.06$ using
Triisopropylindium - from R. Gedridge
Tertiarybutyldimethylantimony - from ATM
Develop a New Bi Precursor
Triisopropylbismuth - from R. Gedridge
Demonstrate Material with 12 μm Band Gap

OTHER APPROACHES:

(111) InAs/InSb Superlattices
Theoretical Calculations Indicate Monolayer
Superlattices Have Band Gaps of < 0.1 eV

